PRESENT STATUS OF THE MOLECULAR FIELD PROBLEM[1]

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INTRODUCTION

When certain general principles began slowly to emerge from the mass of chemical facts available some fifty years ago, it was the classical theory of energy transformations which quite naturally proved the most useful tool for purposes of correlation and giving precision to the developing ideas. Indeed, thermodynamics is a branch of Physics peculiarly suited for the discussion of the complex interplay of the different manifestations of energy change to be found associated with chemical processes.

While thermodynamics proved sufficient for correlating almost the entire range of experimental facts which were formerly considered by the student of chemistry, in our day a wide variety of phenomena has accumulated to a wholly amazing degree. In fact, the theory of the properties of solutions in all states of aggregation, the interpretation of chemical equilibria, and the transformation of chemical energy into electricity included, scarcely twenty years ago, almost the entire range of the subject of physical chemistry. The progress of the experimentalists' art has, however, brought forward a large mass of facts concerning adsorption, catalysis, the colloidal state, rates of reaction, the action of light energy in relation to chemical change, surface tension and spectral characteristics as related to molecular structure, for the understanding of which thermodynamical treatment alone does not go far enough. It is the kinetic theory in an extended form, which promises to provide the most convenient basis for ordering and interrelating these phenomena.

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The kinetic theory of matter has always been, more or less, a subject of serious study by the chemist, but in the period of the development of the earlier physical chemistry the comprehensive and beautiful correlation of chemical facts with the aid of thermodynamics inclined many to the opinion that at least for a very long time, the kinetic theory was to play the rôle of an interesting but somewhat minor adjunct in the development of the science. It is true there were, and still remain, many serious theoretical difficulties to be surmounted in the kinetic theory, in contrast to thermodynamical theory, which, keeping aloof from mechanical hypotheses, is based on absolutely general principles. Nevertheless, the developments of the quantum theory have gone far to remove some of the theoretical difficulties hampering the classical kinetic theory, notably those connected with specific heats, and the recent investigations in "quantum statistics" promises important developments which may soon place the general theory on an entirely satisfactory theoretical basis.

It may be apropos to refer briefly to the nature of some of the more important difficulties which have beset the classical (Newtonian) statistical mechanics. The heat capacities of the monatomic gases appear to have the value predicted by the classical theory, namely $3R/2$. To obtain the latter value, however, it is necessary to neglect the energy of rotation and assume that the molecule possesses no energy other than translatory. Monatomic atoms (or monatomic molecules) are known to possess, however, an extremely complicated internal structure as evidenced, for example, by their spectra; and the question arises as to how the internal energy of the atom can be so completely independent of the energy of translation. Stating the matter in a somewhat different way: how is it that the energy of translation is not lost to the internal vibratory energy of the atoms with an attendant continual diminution of the translatory energy? No satisfactory answer to this problem can be given by a kinetic theory based on Newtonian mechanics. Thus, helium is known to consist of a positive nucleus and two electrons. This should give, counting each component of the translatory energy as contributing $R/2$ calories to the specific heat, a heat capacity of $3R/2$ for the translational energy plus, possibly, $3R/2$ for each particle constituting the atom or $12R/2$ calories as the maximum conceivable heat capacity.

These difficulties in the kinetic theory and others related thereto were known to Maxwell and referred to by Lord Kelvin in his Baltimore lectures as a cloud over the kinetic theory. The quantum theory has done much to clear away the cloud although not with final completeness.

The general quantum theory answer to the difficulty is that there is a lack of analogy between the internal vibratory processes going on within the atom and the translatory motions of the atoms as a whole. The mechanism governing the transfer of energy due to the motion of the electrons constituting the atom (the interatomic and intramolecular energy) to space is controlled by the operation of special laws (quantum dynamical laws) differing completely from the Newtonian dynamical laws, which have been assumed to govern the translatory energy.

The development of these newer dynamical laws has not, however, stopped with their application to the movement of the particles constituting the atom, but considerations of a quantum nature applied to the translatory energy lead to a modification of the deductions relative to a monatomic gas at very low temperatures. The latter problem is still in a state of flux; Einstein and Bose, for example, proposing a form of statistics leading to a perfect gas expression where pressures are predicted to be less than those given by $p = RT/v$ while Fermi-Dirac basing their statistics on the Pauli (1) "dictum" predict a precisely opposite effect.

The situation presented then is briefly that the expanding range of phenomena of special interest to the chemist requires as a medium for discussion and correlation a kinetic theory firmly grounded on a broadened or rather generalized statistics. Richard C. Tolman has well emphasized this in a recent excellent book (2) where an introduction of quantum ideas into the classical mechanics is attempted, rather than the more radical step of Dirac where about the only portion of the older ideas retained is that entropy is assumed proportional to probability; a probability however redefined to incorporate a generalization of the Pauli dictum.

If the chemist were interested alone in the validity of the "perfect gas" equation, he would have little to be concerned about. There is, however, considerably more than this involved in the problems which must be solved in connection with photo-chemical effects, reaction velocities, colloid behavior, the equation of state problem, referring to but a few of the types of phenomena which are of fundamental importance in the science. The main object of the present paper is to call to attention and to discuss in some detail several properties of matter, an accurate experimental knowledge of which would aid substantially in arriving at a decision as to the value of some of the speculative ideas being applied in treating theoretically the various classes of phenomena referred to above. As already suggested the important general problem of particular interest to the physical chemist is that concerned with the development of a kinetic theory having as a basis *generalized* statistics which will avoid the difficulties which have surrounded the classical statistics.

THE MOLECULAR FIELD

The classical kinetic theory was found to suffice to a considerable extent in explaining the range of experimental facts available up to perhaps 75 years ago. It is true that Joule and Thomson's porous plug experiment had indicated that a molecular model of the perfectly reflecting type characterized by mass and velocity, was insufficient to explain the effect obtained with nitrogen and carbon-dioxide or the opposite sign of the effect in the case of hydrogen. Moreover, Regnault's and Andrews' experimental results as well as those of others, made it abundantly clear that the simplicity of the laws of gases was at best a condition which obtains for a gas only at very low pressures. The notion of endowing the classical model with an attractive field had been proposed at various times by various people (3) but no one did anything very seriously about the matter, at any rate in the case of gases, until van der Waals' attempt was presented in the 1873 Essay. Hirn (4) had pointed out some years before van der

Waals' essay appeared that a "cohesive pressure" might aid in explaining the failure of the gas laws (Boyle, Gay-Lussac).

The van der Waals' model consists then of the classical molecular model with the addition of an attractive field of spherical symmetry. The carrying out of the computation of the equation of state by van der Waals for what may be called a "van der Waals' model" was not in all details satisfactory. In fact, it is easy to show that the final equation of van der Waals is accurate only at high temperatures and low pressures for a gas composed of molecules of the van der Waals' type. The principles involved in the general computation are of such importance and interest, and are so often omitted in books treating of physical chemistry, that certain important considerations relative to the van der Waals' model and its treatment will be reviewed.

We may begin by remarking that a molecule whose molecular field is solely attractive seems artificial in view of the need of also imagining a repulsive field to "balance the attraction" (5). The difficulty may be much relieved by considering further the specification of the assumed perfectly-elastic quality of the model. In interaction, or collision, a pair of classical or van der Waals' molecules of diameter d are assumed to develop mutually a large (infinite) repulsive force for distances of separation less than d (the distance between centers) and a force precisely zero for distances in excess of d. The repulsive action may be assumed therefore to take place over an infinitely thin spherical shell surrounding the molecule. Such conditions of interaction would follow if the repulsive force R is put, for example, equal to $\lambda_n r^{-n}$, and n becomes mathematically infinite. Otherwise expressed the van der Waals' model may be viewed as one possessing a repulsive field, the index of which, n, is very large or infinite. The condition of infinite n need not be taken in the literal sense for it will be shown later that $n = 15$ is a practical approximation for mathematical infinity in accounting for the physical properties of certain gases. Assuming the above considerations to remove the difficulty presented by the apparent absence of a repulsive field for a van der Waals' model, the nature and mode of action of the attractive field remains to be considered.

The attractive field for simplicity, may be represented analogously to the repulsive field by $\pi_m = f\,(r^{-m})$. Many have assumed that π_m was simply $\lambda_m\, r^{-m}$ where λ_m is a constant,[2] m ranging from 2 to several times the latter number. Calling into consideration the information now available concerning atomic structure this simplicity seems scarcely acceptable. Leaving this detail aside for the present, however, it will be assumed that π_m is given by $\lambda_m r^{-m}$ and certain limitations of van der Waals' original deduction of the cohesion pressure may be mentioned.

As long as molecular fields are assumed absent the classical theory states that the distribution of the molecules within a given range of velocities will be determined solely by the kinetic energy of motion of the molecules. The presence of either an attractive field or repulsive field, or both, introduces another factor, for it is easily perceived that the probability of "nearness" of two neighboring molecules will be greater in an attractive field and less in a repulsive field. In fact, the probability of a number of molecules possessing a given range in the velocity space, $d\dot{x}d\dot{y}d\dot{z}$, is proportional (classically) to the expression $e^{-\frac{\epsilon}{kT}}$ where ϵ is the kinetic energy of a molecule, k being Boltzmann's constant and T the absolute temperature. Similarly, if $\int \pi_n \, dr = \varphi_n$ and $\int \pi_m \, dr = -\varphi_m$ are the potential energies of repulsion and attraction respectively, the "probabilities of position" may be taken proportional to $e^{-\frac{\varphi_n}{kT}}$ and $e^{+\frac{\varphi_m}{kT}}$. There entering no other types of energy into the consideration, the number of molecules to be found in any part of the generalized gas space (positions at the walls of the containing vessel being excluded) is proportional to the product of the separate probabilities

$$e^{-\frac{(\epsilon + \varphi_n - \varphi_m)}{kT}}$$

It is now clear from this expression that there will be a tendency, due to the attractive field, for the molecules to cluster or

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[2] The notation has been adapted from the paper of J. E. Jones (6).

aggregate, also this latter tendency is opposed by the repulsive field (disaggregation) and increasing kinetic energy. The aggregation tendency, in short, is opposed by the repulsive property and increase of temperature.[3]

van der Waals proceeded differently. He took as a consequence of the assumed finite and invariable molecular diameter, a free path shortening leading, by a not quite valid computation, to $p = \frac{RT}{v - b}$ for the pressure, where b is the fourfold molecular volume. To the latter equation, van der Waals then merely added $- \frac{a}{v^2}$ as a result of general considerations leading from La Place's capillarity theory.[4] Thus, the aggregation effect is not included and since the latter effect is effaced at high temperatures it is evident that van der Waals' deduction may be regarded as possessing greatest validity if applied to a gas at high temperatures (strictly T infinite) and low pressures. The form of the resulting equation happens to be such as to reproduce in a qualitative way the isotherms of a gas-liquid system. The equation has therefore been used to discuss the liquid state which is not strictly legitimate as indicated by the theoretical status of the equation. Indeed the aggregation effect is to be regarded as *one* of the principal factors in bringing about the existence of the liquid phase; an effect as already shown, not included in the van der Waals' equation.[5]

Besides van der Waals' treatment of the molecular field in

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[3] It is to be noted that kT in the probability exponential is equivalent to θ in Gibb's statistical treatment. Gibbs does not make the identification between $\frac{\theta}{k}$ and temperature, contenting himself, at most, by implying that θ is analogous to temperature in the case of a gas.

[4] The use made by van der Waals of La Place's theory may well raise objections since the latter theory is based on the conception of an incompressible fluid and the effect of molecular movement is ignored. In fact the theory even ignores altogether the existence of molecules.

[5] It may indeed be found that the classical mechanics are insufficient to provide the proper basis for discussing quantitatively the conditions insuring the existence of the liquid phase.

the case of the equation of state problem, many (7) (8) (9) (10) (11) (12) (13) (14) (15) have given more exact computations, not alone for the van der Waals' model but for other simple models.

THE ORIGIN OF THE MOLECULAR FIELD

Thus far the existence of a molecular field, attractive or repulsive, symmetrically disposed about the molecular model, has been merely postulated. The origin of such fields is a matter of the greatest importance if further progress in the kinetic theory from the quantitative point of view is to follow. We owe Debye's (16) (17) fertile imagination an explanation, consistent with modern views regarding atomic structure, of the origin of these fields. It is true that the information regarding the structure of atoms and molecules is altogether insufficient at present to permit of the desired quantitative development of Debye's ideas, but it is already clear that these ideas are correct and will serve to guide properly conceived investigations into a path leading in time to a satisfactory understanding of the molecular field. The matter is of so much importance and has been referred to so meagerly in the physico-chemical literature that a brief sketch of Debye's ideas may be apropos in the present paper.

Considering atoms or molecules in any state of aggregation, it is a familiar fact that the dielectric constant and refractive index is greater than for a vacuum. To account for these phenomena it was long ago assumed by Sellmeyer and Helmholtz, for example, that the atoms or molecules possessed charged particles (electrons) bound into positions within the molecule by means of elastic forces: the distance of displacement of the electrons under the action of light or any electric field being assumed proportional to the displacing force acting. Such a simple basis was fruitful in leading to the Lorenz-Lorentz equation $\frac{n^2 - 1}{n^2 + 2}\frac{1}{\rho} = \text{constant}$ where n is the refractive index and ρ the density. The same atomic model suffices to give the Clausius-Mosotti equation $\frac{D - 1}{D + 2}\frac{1}{\rho} = \text{constant}$, where D is the dielectric constant. To assume, therefore, that the electrons composing the atom are immovable under the action of the electric light vector or the electric field amounts to denying the possibility of the refractive index or dielectric constant being different from that of a vacuum. The displacement of the electric charges, or the *equivalent* of a displacement, may accordingly be accepted.

Now a collection of molecules constituted of a positive portion and electrons sufficient in the aggregate of their negative charge to neutralize the positive charge, will exert a mutual electrical influence upon one another. For example, consider the center of electrical effect for the positive electricity to coincide with the electrical center for the negative electricity in a single molecule removed from the action of every similarly constituted molecule or electrical effect. Now bring this molecule whose constituting charges are movable into the presence of one or more similar molecules. The reciprocal effect of the molecules one upon the other (regardless of orientation or kinetic energy) will be to separate the centers of electrical action of the positive and negative charges in each molecule from coincidence, producing thereby an *induced* polarity. The induced polarity may be regarded in every way as similar to that produced by the action of an outside electrical field in the case of the dielectric property or the electric vector of light in the case of the refractivity. Let the induced electrical polarization of the molecule be α and the electric field arising from the electric charges constituting the molecule and inducing the moment be represented by E. Then the electric moment is αE. The work necessary to bring a molecule from a point where the field E_1 is zero into the midst of the gas where the field is E will be $-\ \alpha E\ \frac{E}{2}$ or $-\ \frac{\alpha E^2}{2}$. The quantity α, the induced polarization is therefore proportional to the constant of the Clausius-Mosotti formula, namely $\frac{D-1}{D+2}\ V = \text{Constant} = \frac{4}{3}\ \pi N\alpha$. A computation of the average squared electric field $\overline{E}^2$ in terms of the number and positions of the electric particles composing the atoms will in principle lead directly to an expression for the potential energy between any two molecules or ϕ_m referred to above. $\left(-\frac{3\,\alpha\tau^2}{r^8}\right.$ for quadrupole[6] molecules where τ is the electrical "moment of inertia," i.e., charge × (distance)^2, and r is the distance between the centers of the molecules.$\left.\right)$

The origin of the repulsive field is not quite so easily understood. To illustrate the thought, assume that the electrons move in orbits about a central positive charge as is visualized in the Bohr atomic model (the "reality" of the original Bohr orbits is, on the newer quantum theory, no longer as definitely conceivable). The nature of the effect accounting for the repulsive force may be made definite by considering the example selected by Debye; a Bohr hydrogen atom represented by a positive

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[6] The terms dipole, quadrupole, octapole, etc., are designations which may be applied to molecules when definite positions are assigned to the positive and negative charges of which the molecule (or atom) is assumed to be composed. Thus a Bohr model of the hydrogen atom assumes an electron to be rotating in orbital motion about a positive charge whose magnitude is equal to that of the electron. Such a model may be assumed for certain purposes to resemble in the electrostatic sense a rod charged equally and oppositely at opposite ends. Therefore a dipole. A Bohr model hydrogen molecule on the other hand assumes two electrons opposite one another in the same orbit and revolving midway between two positive charges. There are then four charges in the molecule which may be regarded as forming two dipoles situated relative to one another in a manner to more or less compensate their respective moments and constituting a quadrupole. The simplest model of an octapole molecule would possibly be a positive charge, equivalent to the total charge of eight electrons, at the center of a cube each corner of the cube containing one electron.

It is not improbable that a molecule at small densities might behave as, for example, a quadrupole, and at higher densities differently, as regards polar order due to the mutual electrostatic disturbance which could occur as the molecules become crowded together. Dielectric constant measurements for simple type molecules in the adsorbed state, where they are tremendously "strained," might throw some light on the polarization changes to be expected at high molecular densities. Should considerable changes in polarization be observed in the adsorbed state as compared with the gaseous state, there would seem little doubt that the polar type of the molecule could not be regarded as independent of the density.

charge about which an electron rotates in a circular orbit. The figure represented (fig. 1) the simple negative electron of a hydrogen atom, as equivalent in effect to three hypothetical half charge negative particles and one half charge positive particle rotating about the positive nucleus at opposite ends of the orbit diameter (2a) as represented.[7] From this representation it is clear that the rotating half charge electrons (angular vel. ω) may be considered in their electrical effect, to consist of a negative field associated with which is an oscillating dipole producing a pulsating field at any point without the atomic system (x,y,z). Consider next the nucleus as the center of a coördinate system

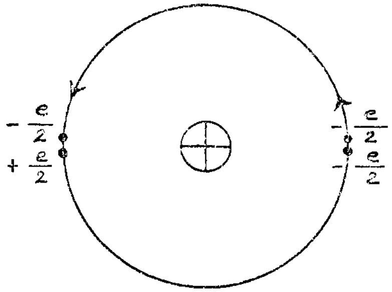

FIG. 1

$(\phi,\ \theta,\ r)$ and fix attention first on the rotating dipole. Taking distances to x, y, z from $+e/2$ as r_1 and $-e/2$ as r_2 there is obtained for the potential at the point $x = r \sin \theta \cos \phi$; $y = r \sin \theta \sin \phi$; $z = r \cos \theta$

$$\Phi_1 = -\left[\frac{1}{2}\frac{e}{r_1} - \frac{1}{2}\frac{e}{r_2}\right]$$

But r_1 is the same as $(r \sin \theta \cos \phi^1 - a)^2 + y^2 + z^2)^{1/2}$
and r_2 the same as $(r \sin \theta \cos \phi^1 + a)^2 + y^2 + z^2)^{1/2}$ where

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[7] I owe this diagrammatic scheme to my colleague, Professor H. B. Phillips. The mode of representation is, of course, purely hypothetical. It is justified only to the extent that the calculation of the potentials of the negative and oscillating fields is facilitated.

ϕ^1 is taken equal to $(\phi - \omega t)$. To a first approximation $r_1 = r - a \sin\theta \cos\phi$ and $r_2 = r + a \sin\theta \cos\phi^1$ whereupon,

$$\Phi_1 = -\frac{ea}{r^2} \sin\theta \cos(\phi - \omega t)$$

which is Debye's equation for the pulsating potential. In a similar way the negative potential ϕ_2 becomes

$$\Phi_2 = \frac{ea^2}{r^3}\left(\frac{1}{2} - \frac{3}{4}\sin^2\theta\right)$$

independent of the time. From the potential the average square of the electrical fields may be computed giving

$$\overline{E_1^2} = \frac{e^2a^2}{r^6}\left(\frac{3}{2}\sin^2\theta + 1\right)$$

$$\overline{E_2^2} = \frac{9e^2a^4}{4\,r^8}\left(1 - 2\sin^2\theta + \frac{5}{4}\sin^4\theta\right)$$

With the Bohr model at a distance $r = 10\,a$ the maximum value of $\overline{E_1^2}$ is 8×10^6 volts/cm. for $\overline{E_2^2}$, 0.76×10^6. It results, therefore, that for this model the amplitude of the field fluctuation is over tenfold the time average field. It is further to be noted that $\overline{E_1^2}$ preponderates more for great distances. The action of the time variable field on an outside electron has been computed and shown by Debye to result in the molecule's exerting on average a repulsive force on the electron. The repulsion of electrons (slow moving) on near approach to molecules is well known experimentally and the considerations reproduced above indicate how this effect comes into existence.

The question of the calculation of the repulsive action of the Debye forces in the case of two atoms or molecules requires evidently a knowledge of the electronic structure in much detail. Meanwhile, however, a considerable step has been taken in comprehending qualitatively how one molecule may reflect another on the basis of the modern electron structure assigned to atoms.

From what has preceded, the necessity is perceived of amplifying and adding to the specifications of the kinetic theory molecule. The molecule must clearly be endowed with both attractive and repulsive forces obeying rather complicated laws. For some purposes or over restricted ranges of the variables, (i. e., temperature, pressure or both) it will possibly often suffice to assume simple inverse distance expressions; but experience alone can indicate to what extent and in which cases such simplifications remain a sufficient approximation in accounting for the various effects connected with molecular collisions or interactions generally.

THE MOLECULAR FIELD IN TRANSPORT PROBLEMS

The transport problems of the kinetic theory, viscosity, heat conduction, and diffusion are represented by the transfer, through the collisional phenomena, of momentum, energy and mass. Of the three the viscosity effect is of particularly great interest since it can be most easily measured accurately over a long temperature range.

A complete transport theory for other than the classical molecular model is complicated. The complication involved turns very largely on the fact, however, that we are ignorant of the law of molecular distribution for a gas in a steady state undergoing viscous action, as distinguished from a gas in the equilibrium state. Thus the Maxwellian distribution cannot be assumed to hold, for this law applies only to the case of a gas *in equilibrium*.

The classical molecular model was shown by Maxwell to lead to the prediction, somewhat surprising on first consideration, that the viscosity of a gas is independent of the density. This Maxwell himself proved experimentally.[8] A further prediction, however, was that the viscosity varies as the square root of the absolute temperature. The latter prediction has been found emphatically not to be in accord with the facts for any gas at any temperature range thus far investigated.

The difficulty of the temperature dependence appeared to be

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[8] Boyle observed in his day that the time of oscillation of a pendulum was independent of the density of the air in which it was caused to operate which would be the case only if the viscous drag on the pendulum were independent of the density of the ambient air.

solved when the viscosity formula for a van der Waals' molecular model was computed by Sutherland (18) leading to a temperature dependence representable by $\frac{\sqrt{T}}{1 + \frac{C}{T}}$. The quantity C represents a quantity which is directly proportional to the work required to separate two molecules, of the hard sphere type, from contact to infinity. It is therefore closely related to the quantity a in van der Waals' equation.[9] This has been shown in recent papers (19) (20) where the relation of C and a to the dielectric constant has been discussed.

If instead of a molecule of invariable diameter (index of repulsive force infinite) the viscosity formula is obtained for a molecular model possessing both repulsive and attractive fields the formula (6) has the form

$$\frac{\sqrt{T}}{\frac{1}{T^{\frac{2}{n-1}}} + \frac{C'}{T}}$$

where C' has the same physical significance as the coefficient C in the Sutherland formula. It may be noted that for n infinite in the more general formula there results the Sutherland form based on the hard sphere model.

The subsequent perfection attained in the experimental results for many gases combined with the extension of the measurements to lower temperatures, however, has shown two things. Firstly, the Sutherland formula fails to represent the viscosity data for many gases as lower temperatures are approached and secondly in the case of helium (21) it fails completely at all temperatures.

The general need of considering the molecular field in the theory of viscous action thus becomes evident. In fact, Maxwell himself had perceived that the difficulty of the temperature dependence resided in greater part, in the failure to take account of a

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[9] The a values with which C must be compared cannot in general be a as determined from critical constants but a value obtained from the gaseous compressibility data.

"molecular field effect." He developed the general equations for transfer phenomena, investigating, however, only the special case of points repelling as the inverse fifth power of the distance; an assumption which enabled him, due to the form of the fundamental equation, to dispense with a knowledge of the molecluar distribution law. We owe to Enskog (22) (23) (24) and Chapman (25) the important results obtained by carrying the theory of gaseous viscosity to a definite and complete solution for each of the three molecular models; viz., the classical model, the van der Waals' and the point model repelling according to the formula $\lambda_n r^{-n}$. A further case has been partially investigated by Jones (6) who considers a molecule represented by a point and possessing both attracting and repelling fields of the type $\lambda_m r^{-m}, - \lambda_n r^{-n}$. It is sufficiently shown in the latter investigation that all the known facts concerning the temperature dependence of viscosity can be accounted for, if not entirely satisfactorily from a quantitative point of view, at least qualitatively. The position at present reached is then clearly that in general *both* the attractive field and the repulsive field must be considered in the kinetic theory. A final satisfactory knowledge of the molecular field depends, however, on a considerable extension of our knowledge of atomic and molecular structures combined at the same time, of course, with the discovery and development of a generalized dynamical theory.

DIELECTRIC CONSTANTS

Twenty years ago few physical chemists would have believed the special study of dielectric constants to have any direct relation to the major problems of their science. At present, however, there exists almost a "furor" for measuring the dielectric constants of gases and liquids which may readily be justified. The most important recent contribution to the theory of solutions (Debye-Hückel theory) makes considerations of the dielectric qualities of the solution system of fundamental importance, although for gases alone does a clear theoretical status exist. The interesting and important work on organic liquids at present being carried out, while as yet in many aspects uninterpretable theoretically, is nevertheless destined ultimately to have far reaching consequences.

The comments above have indicated that the cohesive pressure or the molecular attractive field is for quadrupole molecules, directly proportional to the Clausius-Mosotti constant. $\left(\frac{D-1}{D+2}V = \frac{4}{3}\pi N\alpha = P_0.\right)$ In two recent papers (19) (20), the present writer has shown empirically that the constants for normal substances are simply related to the A and β constants of the equation of state and heats of adsorption. The characteristic of some molecules (polar compounds) of possessing a natural or permanent moment is of very great importance and the development of the theory by which the numerical values of the molecular dipole strength can be determined is of fundamental interest in enlarging the boundaries of the kinetic theory. A brief review of the physical ideas underlying the present theory is accordingly presented.

The theory of gaseous dielectric behavior which is most elegantly substantiated by the available experimental data is that of Debye, (26) (27) (28). The original theory was wholly classical in its theoretical setting. The subsequent attempts to give the theory a proper quantum "baptism" have been numerous, finally culminating in Pauli's treatment of the problem by the matrix mechanics which results in an expression reducing for higher temperatures to Debye's original formula.

The Debye theory is based on simple, physical ideas. The experimental data indicated long ago that substances, in their dielectric behavior, may be classified into two groups, those for which the function $\frac{D-1}{D+2}V$ (Clausius-Mosotti expression) (D dielectric constant, V molecular volume) is constant and those for which it is not. Now the theory leading to the expression $\frac{D-1}{D+2}V = \text{constant}$ is readily derivable, assuming the presence of a movable electron in the molecule and that the external electric field in which the gas is brought induces an electric moment in the molecules composing the gas. Proportionality between the induced polarization of the molecules and all values of the field strength is also assumed. Debye gave the solution of the following problem: assume a molecule capable of becoming inductively polarized and superpose thereon the effect, in the actual state of movement of the molecules as conceived in the gaseous state, a *permanent* or *natural* dipole moment having a fixed position in the molecule. It is clear that in an electric field the latter kind of molecules will tend to align themselves in the field with the axis of the natural moment in the direction of the field. But the aligning tendency is interfered with the higher the temperature becomes because of the motion and collisions of the molecules. Thus for very high temperatures the aligning tendency would be almost completely destroyed. The contribution, therefore, of the natural dipole to the dielectric constant formula should be representable by a term or terms containing inverse temperatures. A formula containing a first approximation for the *dipole* term would be given by the following expression:

$$\frac{D-1}{D+2}V = \text{constant} + \frac{a}{T}$$

The computation of a, using the ordinary probability theory (29) to calculate the number of molecules whose axes make an angle in the range $d\theta$ with the field direction, gives $a = \frac{4}{9}\frac{\pi N\mu^2}{k}$ where N is Avogadro's number, μ the value of the permanent natural electric moment and k Boltzmann's constant.

Exactly what character of atomic structure can lead to a natural electric or dipole moment is not known, otherwise it would be possible to compute μ. Meanwhile values of a may be determined from observational material and μ computed. The values of μ thus obtained are largest for hydrochloric acid gas, water, the alcohols, and in general a temperature dependence of the Clausius-Mosotti expression is found for those substances which, from certain aspects of their chemical behavior, chemists had long ago designated as "polar" compounds or "associated" compounds.

With the assistance of a knowledge of the magnitude of the permanent moments it is possible to construct a purely electrical theory for the representation and correlation of the facts concerning certain liquid mixtures (associated substances) such as, for example, the freezing points and boiling points. Such a theory may be viewed indeed as a logical extension of the well known Debye-Hückel theory of ionic solutions. A few details regarding the treatment of liquid mixtures from this point of view are to be found in Debye's article on "Dielectric Constants and Association" in the sixth volume of the Marx's Radiology. The present paper merely calls attention to the fact that a further development of the theory of non-aqueous solutions from the point of view suggested by Debye cannot fail to be more satisfactory, more general and fruitful in guiding further experimental research in a profitable direction than the special explanations hitherto advanced to explain certain "anomalies" in liquid mixtures.

THE REFRACTIVE INDEX AND SCATTERING OF LIGHT

The older classical theory has already been referred to in relation to the refractive index in the discussion of which it is sufficient for purposes of orientation, to assume merely that the electrons in the molecule are displaceable from their equilibrium positions under the action of the external forces. The theory of such effects as ordinary dispersion and anomalous dispersion offers difficulties, however, when the assumption is made that the electrons are moving in orbits, for here we do not have equilibrium positions for the electrons. It may be assumed, nevertheless, that a perturbation or shifting of the orbits takes place due to the action of the light or an electric field although the precise details are complicated by the mutual inter-relation of the other orbits. In a simple case it is readily perceived that the deviation or wobbling of the orbit from its original form will constitute a virtual electric moment and the observable effects of the action of light produced in gases may be assumed due to the rate of change of a virtual electric moment. The relation of refractivity to the dielectric constant is important and in many gases ("non-polar") the index of refraction for long wave lengths is equal to the square root of the dielectric constant.

A theory of dispersion has been developed by Debye (30) for the case of the Bohr hydrogen molecule on the basis of a periodic wobbling of the orbits responsive to the external periodic force of the electric vector of the light beam. Debye deduces from this periodic disturbance of the original motion of the electrons, the index of the refraction of hydrogen as a function of the wave length. On comparison with experiment (31) it is found that the calculated index is in agreement for wave lengths in the visible regions but there occurs a progressive deviation at shorter wave lengths. In the ultra-violet region the deviations are considerable, which might be expected in view of the limitation of infinitely small disturbance of the orbits assumed in computing the refractive index formula. Moreover, it is well known that in the ultra-violet absorption takes place disrupting the hydrogen molecule. The classical basis upon which the calculations rest would of course cease to be sufficient as a basis for discussing the phenomena when absorption takes place. In fact it is precisely the matter of absorption which has constituted a grave difficulty in the older theories and which constitutes an even more formidable difficulty in considering the phenomena on the basis of Bohr's model. It is true Bohr has given, for his molecular model, some noteworthy explanations of absorption particularly for those special cases of resonance and fluorescence.

One remark should be added concerning Debye's formula for the refraction of hydrogen. The formula for $(n^2 - 1)$ contains several terms of which three have the form $Ne^2 / m (\nu_o^2 - \nu^2)$ where the denominator contains the difference between the square of the incident frequency and ν_o^2 a quantity characterizing the vibrations of the molecule. There are, however, two more terms in which instead of the difference of two frequencies there enters the *sum,* showing that they correspond to degrees of freedom for which the motion is *unstable* (32). Lorentz (33) has given expression to the difficulty by stating "it is just as if you wanted a pendulum to vibrate about a position of unstable equilibrium in which it stands vertically upward." Attempts to improve the theoretical position of the subject have been made recently by several European investigators. (34) (35) (36) (37) (38) (39) (40) (41).

The so called scattering of light is closely related to the dispersion problem as discussed above for which Rayleigh deduced (assuming the molecules to constitute a perfect gas) the well known formula,

$$h = \frac{32\ \pi^{+3}}{3} \frac{(n^2 - 1)^2}{N\ \lambda^4} = - \frac{dI}{Idx}$$

where $\frac{dI}{I}$ is numerically the percentage change in the intensity of the beam of light when traversing a layer of unit thickness. Since h varies inversely as λ^4, the scattering will increase in the direction of smaller wave lengths; an effect which as we well know accounts for the blue color of the sky. The theory of the scattering for long waves[10] may be given in a quite different form in which the basis of the consideration involves essentially the use of the ordinary probability theory in computing the fluctuations in density of the gas. Since the refractive index varies with density the gas is to be regarded as inhomogeneous for a periodic disturbance such as light. Scattering of the light thus occurs and the Rayleigh formula is again obtained with, however, the important difference that the von Smoluchowski's (42) expression is more general not being restricted to a perfect gas. It can therefore be applied to the critical condition of a fluid, providing an explanation of the critical opalescence.

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[10] "Long waves" refers to a magnitude large as compared to the average distance between molecules in a substance. Thus green light is of wave length 5600 $\times 10^{-8}$ cm. whereas in a gas at 0° and one atm. the average distance of the centers of molecules is 33.3×10^{-8} and the condition of "long waves" is therefore fulfilled. In a regular crystal, the even spacing of the molecules would produce no scattering (transparency) until the wave length of the incident light became of the same order of magnitude as the distance between atomic centers (2 to 3×10^{-8} cm.). Waves of such length are obtained from the x-ray tube which give scattering from crystal planes, the intensity of which is exceedingly strong in definite directions as first shown by Laue.

The aspect of light scattering phenomena of most interest to the physical chemist is connected with the polarization relations of the incident and scattered light. According to the original Rayleigh theory a plane polarized incident beam should be accompanied by plane polarized light in the scattered light. If, on the other hand, the incident beam is heterogeneous the scattered light will be partially polarized, yielding two components each of equal mean intensity. The observation of the actual polarization discloses, however, that this is true for but few gases leading to the inference that the molecule is not electrically spherically symmetrical. Thus argon and neon show the simple behavior predictable from Rayleigh's formula, thereby implying a high degree of symmetry in the electronic structure of these atoms, whereas helium appears to be unsymmetrical.

Under the circumstances the obvious addition to make to the theory is to assume, in a phenomenological manner, that the molecule possesses a different electric moment, responsive to the light vector for each axis (m_x, m_y, m_z). The molecules will evidently orientate in every direction in the course of their movements in the gaseous state and by a somewhat more complicated procedure than Rayleigh employed there results a general formula, which for incident light propogated along the z axis, gives for the ratio of the intensity of the light parallel to the incident beam (S_p) to that perpendicular to the incident beam (S_s) an expression which depends on b_{11}, b_{22}, b_{33}, the principal "anisotropic" coefficients of the molecular moments corresponding to the axes x, y, z. Thus designating by R (43) the ratio of S_p to S_s, there results the equation:

$$\frac{10\,R}{6\text{–}7\,R} = \frac{(b_{11} - b_{22})^2 + (b_{22} - b_{33})^2 + (b_{33} - b_{11})^2}{(b_{11} + b_{22} + b_{33})^2}$$

an expression which vanishes for $b_{11} = b_{22} = b_{33}$ (i.e., a molecule symmetrical in the sense proposed). A few data are given in table 1 taken from Debye's article in Marx Handbuch der Radiologie.

The result of surprising interest is that helium shows a defect in symmetry larger than for any of the other gases of the table.

The fact that for N_2, R is twice that for CO is significant of a difference which would not have been inferred since these two gases show a surprisingly close parallelism in their physical characteristics. Benzene is more asymmetrical than might have been supposed by one familiar with its organic chemical properties.

Clearly the scattering of light should be further investigated for a wide variety of substances since the phenomenon affords a very direct approach to an enlarged knowledge of molecular anisotropy. Thus the organic compounds have been assigned very definite molecular structures which should be related (44) to the indications regarding molecular character deducible from light scattering data.

TABLE 1

SUBSTANCE	$Sp/Ss = R$
H_2	0.022
He	0.42
A	0.00
Ne	0.01
N_2	0.037
O_2	0.064
C_2H_2	0.12
C_6H_6	0.06
NO	0.026
N_2O	0.122
CO	0.017
CO_2	0.098

ELECTRIC DOUBLE REFRACTION IN GASES AND LIQUIDS

Kerr, some fifty years ago, found that carbon bisulfide became double refracting for a light ray perpendicular to an electrostatic field in which the liquid was placed. The amount of the effect was shown by Kerr to vary as the square of the field strength. The analogous effect in the magnetic case was observed by Cotton and Moulton (45). The experimental arrangement for demonstrating the effect consists essentially of a pair of metal plates with means of applying a potential, and a pair of Nicol prisms. In figure 2 the plates + and − are introduced into the carbon bisulfide and a ray of plane polarized light passed through the liquid parallel to the metal plates. One of the Nicol prisms, n_1n_1, is placed before the plates, the other, n_2n_2, after the plates in such a way that the principal planes of the prisms are included at 45° to the field direction. With such an experimental arrangement no light will pass in the absence of a field with an isotropic liquid between the plates. Kerr found that light would pass when an electric field was established between the plates thus demonstrating a state of "electric strain" suffered by the molecules under the action of the field. The magnitude of the double refraction has been found to diminish greatly with temperature increase.

The type of theory which is at present in best accord with the experimental facts makes use of the Langevin orientation theory

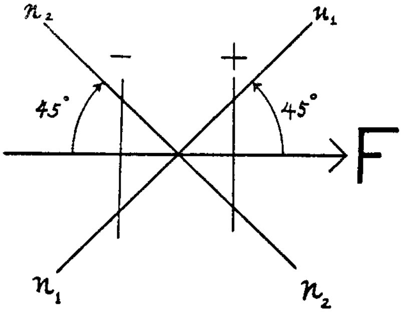

FIG. 2

(29) with a polarizable molecule assumed to have different properties in different directions. Two cases are distinguishable, that in which the molecules are susceptible of an inducing action of the field and electric vector of the light beam only, and that in which the latter effect is combined with the effect due to a natural dipole analogously as in the theory of dielectric constants. The theoretical mode of treatment is statistical and the classical probability theory has been used with the assumption that the molecules are completely anisotropic (for illustration, a flattened ellipsoid as compared with the sphere). The relation of anisotropy to molecular structure is a subject about which much remains to

be learned, moreover the development of the theory of the Kerr effect deserves continued attention (46) (47) (48) (49).

The general formula for the Kerr effect is as follows, where K is the constant, n_p the index of refraction for the ray vibrating perpendicular to the field. The index of refraction for the normal liquid (wave length λ) may be denoted by n_o and the field intensity by E.

$$\frac{n_p - n_s}{n_o} = KE^2 = B\frac{\lambda}{n_o}E^2 \tag{1}$$

$$K = B \text{ (a constant) } \lambda/n_o$$

The theoretical problem centers on the computation of the indices n_p and n_s and, as already stated, the model of the molecule which appears to be fairly satisfactory is that which is assumed to be polarizable differently in different directions, and, in the general case, possesses in addition a natural dipole moment.

The effect brings into evidence the fact that molecules are not spherically symmetrical in structure and this constitutes the reason for the special interest of the phenomena for physical chemistry. There are several aspects of this special interest, but the more obvious are perhaps the assistance a wide range of data for many substances will give, in supplying a definite and quantitative basis for the development of ideas regarding the forces which determine molecular structure and the molecular field. Evidently, it would be well to have also, for completeness, data regarding light scattering, dielectric constants, compressibilities and refractive indices. In recent years data regarding dielectric constants have been accumulating rather rapidly and to a lesser extent in the case of compressibilities. The data should be obtained over a wide range of temperature and density to be of maximum usefulness for theoretical purposes.

Returning to the fundamental formula of the Kerr effect, it will be useful in giving definiteness to the nature of the present theory to write down the expressions for n_p and n_s. Note should be made that the sign of the effect may be + or − or zero accordingly as $n_p > n_s$, $n_p < n_s$, $n_p = n_s$. For the refractive index of the substance before applying the field, n_o, there exists the formula of Lorentz

$$\frac{n_o^2 - 1}{n_o^2 + 2} = \frac{4\,\pi}{3} N_o \frac{b_{11} + b_{22} + b_{33}}{3}$$

where N_o is the number of molecules in unit volume and b_{11}, b_{22}, b_{33} are the coefficients[11] of the components of the polarizability of the molecule for the *light vector.*

For the ray vibrating parallel to the static field, n_p, and perpendicular thereto, n_s, there may be written

$$\frac{n_p^2 - 1}{n_p^2 + 2} = \frac{4\,\pi}{3} N\, P_z$$

and

$$\frac{n_s^2 - 1}{n_s^2 + 2} = \frac{4\,\pi}{3} N\, P_x$$

The expressions for P_z and P_x are as follows (43) where Z_o is the strength of the static field:

$$P_z = P_o + (\theta_1 + \theta_2)\, Z_o^2$$

$$P_x = P_o + \frac{1}{2}\, (\theta_1 + \theta_2)\, Z_o^2$$

where $(b_{11} + b_{22} + b_{33})\ /\ 3 = P_o$ and θ_1 and θ_2 have the following significance, μ_1, μ_2 and μ_3 being the components of the natural dipole moment.

$$\theta_1 = \frac{1}{45\,kT}\,[(a_{11} - a_{22})\,(b_{11} - b_{22}) + (a_{22} - a_{33})\,(b_{22} - b_{33}) + (a_{33} - a_{11})\,(b_{33} - b_{11})]$$

$$\theta_2 = \frac{1}{45\,k^2T^2}\,[(\mu_1^2 - \mu_2^2)\,(b_{11} - b_{22}) + (\mu_2^2 - \mu_3^2)\,(b_{22} - b_{33}) + (\mu_3^2 - \mu_1^2)\,(b_{32} - b_{11})]$$

There remains to consider the phenomenon of the volume change (or change in N_o) which may take place when a fluid is placed in an electric field (or magnetic field). The expression

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[11] The analogous coefficients for the molecular polarizability due to the static electric field are denoted by the symbols a_{11}, a_{22}, a_{33}.

for the volume contraction is determined, aside from the strength of the field E by the change of the dielectric constant with pressure (50) and is as follows:

$$\frac{dv}{v} = \frac{1}{2}\left(\frac{dD}{dp}\right)_T \cdot E^2$$

The density of the fluid through which the light is passed in the Kerr experiment is therefore not constant but changed in proportion to the square of the strength of the field. Taking into account this fractional change in the number of molecules between the plates, the expression for 1 becomes

$$\frac{n_p - n_s}{n_o} = \frac{E^2}{36}\,\frac{(n_o^2 - 1)\,(n_o^2 + 2)}{n_o^2}\,\frac{(\theta_1 + \theta_2)}{P_o}\,(D + 2)^2 = K\,E \qquad \text{(A)}$$

The data available to 1920 has been collected and discussed from the point of view of their relation to chemical constitution by Kauffmann (51) and Leiser (52). For the purposes of the present paper it will be sufficient to refer to a few of the data for typical substances (see table 2).

It will be noted that for chloroform and aniline the constant is negative. The sign of the effect may be discussed from the point of view afforded by the equations for θ_1 and θ_2. In the first place if no natural moment exists ($\mu_1 = 0$, $\mu_2 = 0$, $\mu_3 = 0$) the sign will depend upon θ_1 alone. The constant K depends then on a function of the a and b coefficients. It may be that these two coefficients are not very different (or proportional) numerically, at least in a region far from an absorption band. In the latter case θ_1 is a function of squares which means K will always be positive. In general a negative sign indicates that certain numerical relationship exists between the μ and b in the θ_2 expression.

The magnitudes of the average natural moment μ computed from the equation A, agree well with the similar quantity computed from the temperature dependence of the dielectric constant. Thus for HCl the Kerr constant gives 1.04×10^{-8} E.S.U. as against 1.03×10^{-8} E.S.U. from dielectric constant data.

Special interest attaches to an experimental method used by Pauthenier (53) whereby the field is applied and the light beam passed through the liquid simultaneously and in a time of the order of 10^{-6} to 10^{-7} sec. Now the density change in the liquid, due to the static field, requires a time for establishing itself which is measured by the speed of sound in the fluid. It is possible, therefore, to arrange the experiment so that the period of the application of the field and the duration of the light is far less than the time for effecting a density change due to the field. The Kerr constant is under these circumstances given by a simpler expression than A wherein D is absent.

TABLE 2

SUBSTANCE	$K \frac{\overline{\text{cm}^3}}{\text{Ergs}} \times 10^{12} \frac{20°}{\lambda = 5893}$	D
N_2 (gas)	Negligible	Slightly greater than one
O_2 (gas)	Negligible	
NO (gas)	Negligible	
CO(gas)	Negligible	
CO_2 (gas)	24	
NH_3 (gas)	59	
SO_2 (gas)	167	
CH_3Cl (gas)	545	
CH_3Br (gas)	820	
$CHCl_3$ (liquid)	−12.2	4.8
C_6H_6 (liquid)	2.15	2.3
$C_6H_5CH_3$ (liquid)	2.73	2.4
C_6H_5Cl (liquid)	32.7	5.7
C_6H_5Br (liquid)	32.7	5.2
$C_6H_5NH_2$ (liquid)	−4.4	6.9
$C_6H_5NO_2$ (liquid)	+12.2	37.0
H_2O	14.4	80.5
CH_3OH	3.5	51.2
C_2H_5OH	2.8	25.8
C_3H_7OH	−9.1	22.2
Benzyl Alc	−55.8	13.0
CH_3COOH	17.8	

The case for double refraction in a magnetic field is in every respect similar to that ot the static electric field.

COMMENTS ON THE EQUATION OF STATE PROBLEM

In the preceding part of the paper the attempt has been made to indicate the importance to Physical Chemistry of a knowledge of the molecular field. Various physical properties not usually considered by the physical chemist have, therefore, been briefly discussed because of the intimate connection which exists directly and indirectly between the important problem of the molecular field and these phenomena. As a concluding part of this paper a brief review of the Equation of State theory for pure gases will be presented. The latter problem is of fundamental practical importance and a brief discussion will illustrate the fundamental rôle that the molecular field plays in the theory. In addition, the relation of a few of the available experimental facts to the theoretical development will also be reviewed. This is the more important for the reason that by a careful consideration of the limitations of the theory of the equation of state in evaluating molecular constants from observational data, it becomes possible to interrelate the constants of the equation of state for gases to other fundamental physical constants, thus aiding in building up a better theoretical structure and decreasing the range of experimental data required for determining the molecular constants.

The limited range of the validity of the van der Waals' equation has already been touched upon and is indeed well known. These limitations, originate, as already indicated, from the use of an over simplified molecular model and a theoretical treatment leading to results valid at high temperatures and low pressures only. The van der Waals' equation, therefore, cannot possibly be expected to apply to actual substances in the liquid state, the critical state, or the highly compressed gaseous state. The precise meaning that should be attached to the constants a and b *determined from critical data* is in consequence by no means clear. The numerous attempts, therefore, to interrelate the a and b constants to molecular structure or other physical properties may be viewed as unpromising. Indeed, those apparent regularities which have been published, relating the constants a and b

to quantities deduced from other physical properties must be regarded as having little or no clear theoretical significance.

Admittedly, one of the outstanding theoretical difficulties at present confronting the physical chemist, is the doubtful *general* validity of classical statistical mechanics: probably, even when applied to problems involving only the energy of molecular translation. Nevertheless, there is an accumulation of evidence to indicate that at higher temperatures, the classical statistics are very approximately valid. As an illustration consider the recent Fermi (54) expression for a perfect gas at high temperatures,

$$pV = RT\left[1 + \frac{h^3N}{16\,(\pi\, m\, k)^{3/2}} \cdot \frac{1}{T^{3/2}\, V} + \ldots\right]$$

Taking helium and using units of cc. per g., atm. there is obtained for the per cent deviation from the classical expression

$$\frac{p\,\bar{V} - RT}{RT} = \frac{70}{T^{3/2}\, V}\, 100.$$

At zero and one atm. the value of the deviation would be 2.8 × 10^{-4} per cent. At low temperatures the departure of the "Fermi" ideal gas from the classical ideal gas is marked, the pressure being given by an expression of the form

$$p = \frac{a}{V^{5/3}} + \frac{b\,T^2}{V^{4/3}}$$

where a and b are constants. Thus the pressure will vanish only for v infinite at $T = 0$, otherwise a positive pressure exists. This implies that the energy is finite at absolute zero and the heat capacity at constant volume vanishes at zero.

The expectation may be entertained, therefore, that the classical statistics may be applied where high temperatures are in question and higher molecular weight substances[12] are concerned.

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[12] The expression for the deviation of the "Fermi" perfect gas from the classical varies inversely as the $(\text{mol. wt.})^{3/2}$. This would mean a very large deviation for a so-called "electron gas" and correspondingly higher temperatures would have to be considered for negligible deviations from the classical perfect gas state.

When, however, the liquid phase is formed it is by no means clear that the classical mechanics will suffice even if the calculation of the equation of state for such a highly condensed phase could be carried out.

There are several methods (7) (9) (10) (13) (14) (55) (56) (57) of using the classical mechanics to deduce the equation of state, all of which are, from a theoretical point of view, equivalent. The use of the Gibb's equations of statistical mechanics, however, appears to make somewhat more evident the nature of some of the approximations which must inevitably be made in securing a definite result from such calculations. The equation 93 of Gibbs may be made the starting point,

$$\int \dots \int e^{\frac{\psi - \epsilon}{\theta}} \, dp_1 \dots dq_n$$

where ψ may be considered a constant for a definite or constant value of θ. The latter quantity will be assumed equal to kT where k is Boltzmann's constant and T the absolute temperature as defined by a gas thermometer employing an actual gas, where the temperature readings are obtained by conducting measurements in such a manner as to give, by extrapolation, readings referred to the gas at infinitely low pressures. The quantity ϵ is the energy of a molecular system while the p's and q's represent the momenta and coordinates of the molecules characterized by values of ϵ, ψ and θ. The equation 93 integrated over all the phase-space must give the total number of molecular systems and accordingly it is permissible to write (Gibbs Eq. 105).

$$e^{-\frac{\psi}{kT}} = \int \dots \int e^{-\frac{\epsilon}{kT}} \, dp_1 \dots dq_n \tag{1}$$

Gibbs shows that ψ may be identified with the free energy defined by the thermodynamical equation $F = U - TS$ where U is the internal energy and S the entropy. There results finally the equation for the free energy which may be written as follows:

$$\psi = -kT \log \int \dots \int e^{-\frac{\epsilon}{kT}} \, dp_1 \dots dq_n \tag{2}$$

The equation of state follows at once from this equation, provided the indicated integrations can be effected, since $\left(\frac{\partial \psi}{\partial v}\right)_T = -p$. The integrations will be affected for two cases, one in which the van der Waals' molecular model is assumed where the attractive force[13] is represented by $\lambda_m\ r^{-m}$ and also for a point molecule possessing a spherically symmetrical repulsive field $-\lambda_n\ r^{-n}$.

We begin the calculation of the integral by allowing the momentum increment dp of each molecule to be represented by $m^3\ d\dot{x}d\dot{y}d\dot{z}$, ϵ, by $\frac{1}{2}\ m\ (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + (\phi_m)$, where $\dot{x}$, $\dot{y}$, $\dot{z}$, are the velocity components and ϕ_m is the potential energy due to the attractive field (van der Waals' molecular model). The free energy equation then becomes

$$\psi = -\ kT \log \left[(2\ \pi\ mkT)^{\frac{3\,N}{2}} \int \ldots \int e^{-\frac{\varphi_m}{kT}}\ dx_1\ dy_1\ dz_1 \ldots \right] \tag{3}$$

where the dq's have been replaced by $dxdydz$.

The treatment of the remaining integral requires that ϕ_m shall be known as a function of x, y, and z, and due allowance must also be made for the fact that certain portions of the space V containing the molecules are excluded because of the finite volume, $\frac{1}{6}\ \pi d^3$ or δ of each molecule. The gas will be assumed sufficiently dilute that only double collisions need be considered.

$$\int \ldots \int e^{-\frac{\varphi_m}{kT}}\ dx_1\ dy_1\ dz_1 \ldots = \int \ldots \int \left[1 + \left(e^{-\frac{\varphi_m}{kT}} - 1\right)\right] dx_1\ dy_1\ dz_1 \tag{4}$$

Consider the molecules to be introduced into the volume V one at a time. For the first molecule it is clear that no portion of the space requires exclusion since the whole volume is available for its action and no potential energy is involved. The second molecule added to the space finds a portion of the space excluded and the potential energy enters the consideration.

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[13] Reference has already been made to the fact that the molecular field cannot, on the basis of what is already known about atomic and molecular structure, be represented by a single inverse distance expression. Several terms may be necessary depending on the substance and the nature of the phenomena to be accounted for.

Regarding one of the two molecules as a point and the other as of diameter $2d$ it is perceived that the space to be excluded for the action of the two molecules is $\frac{1}{6}\pi(2d)^3$ or $\frac{4}{3}\pi d^3 = 8\delta$. The third molecule added results in $2 \times \frac{4}{3}\pi d^3$ being excluded from the whole volume and similarly for the remaining molecules to the N minus first. The integral in (4) with these considerations applied becomes, if for brevity, the integral

$$\int\left(e^{-\frac{\varphi_m}{kT}} - 1\right) dx_1\, dy_1\, dz_1 \ldots.$$

is denoted by I;

$$V\,[V - (8\delta - I)]\,[V - 2\,(8\delta - I)]\,[V - 3\,(8\delta - I)] \ldots [V - (N-1)\,(8\delta - I)]$$

The expression for (3) is now written:

$$\psi = -kT \log\left(2\,mkT^{\frac{3N}{2}}\right) - kT\,\{\log V + \log\,[V - (8\delta - I)] + \ldots. + \log\,[V - (N-1)\,(8\delta - I)]\} \qquad (5)$$

The value of p is easily obtained from (5) with the following result:

$$p = kT\left[\frac{\partial}{\partial v}\log V + \frac{\partial}{\partial v}\log V\left(1 - \frac{8\delta - I}{V}\right) + \ldots. + \frac{\partial}{\partial v}\log V\left(1 - \frac{(N-1)\,(8\delta - I)}{V}\right)\right] = \frac{NkT}{V} - \frac{N^2kT}{2\,V^2}\,(8\delta - I)$$

The evaluation of I requires that φ_m be given in terms of the distance between two molecules and Debye's molecular quadrupole potential $-\dfrac{3\,\alpha\tau^2}{r^8}$ may be assumed. The integral I becomes, where the integration is to be carried out from the smallest distance of approach (d) to infinity,

$$I = \int\left(e^{\frac{3\alpha\tau^2}{r^8}} - 1\right) dv = 4\,\pi\int_d^\infty\left(e^{\frac{3\alpha\tau^2}{r^8}} - 1\right) r^2 dr.$$

The evaluation of the integral is easily accomplished by expanding the exponential term with the result

$$I = \frac{4\cdot 3\,\pi}{5}\,\frac{\alpha\,\tau^2}{d^5}\cdot\frac{1}{kT} + \ldots..\;\frac{4\cdot 3^{\mathrm{i}}\,\pi}{\mathrm{i}\,!\,(8\mathrm{i} - 3)}\left(\frac{\alpha\,\tau^2}{d^5}\right)^{\mathrm{i}}\left(\frac{1}{d^3}\right)^{\mathrm{i}-1}\frac{1}{(kT)^2} \qquad (6)$$

The final equation for p is, writing for Nk the symbol R, β for $4(N\delta)$, the fourfold volume of all the N molecules,[14] and A for $\frac{6\ \pi N^2 \alpha \tau^2}{5\ d^5}$

$$p = \frac{RT}{V} + \frac{RT}{V^2} \left[\beta - \frac{A}{RT} \left\{ 1 + \frac{25}{78} \frac{A}{\beta\ RT} \cdots + \frac{5^i}{i\,!\,(8i-3)\,3^{i-1}} \left(\frac{A}{\beta RT} \right)^{i-1} \right\} \right] \tag{7}$$

The bracketed member of the third term of the right member represents the "aggregation effect" or "clustering tendency" of the molecules which only becomes negligible at high temperatures. Neglecting the series terms the equation may also be written as follows:

$$p = \frac{RT}{v - \beta} - \frac{A}{v^2}$$

which is the van der Waals' form.

The derivation given may be regarded as entirely rigorous under the conditions assumed, namely the validity of the classical mechanics and not too high pressures. It remains to indicate briefly how this equation corresponds with the experimental facts. We may begin by writing the equation in a somewhat different form where $f\left(\frac{1}{T}\right)$ represents the series terms of the brackets in (7);

$$pV = RT + RTB\,\frac{1}{V} = RT + \frac{RT}{V}\left[\beta - \frac{A}{RT}\left(1 + f\,\frac{1}{T}\right)\right]$$

$$B = \beta - \frac{A}{RT}\left(1 + f\,\frac{1}{T}\right) \tag{8}$$

The coefficient B has been referred to by continental writers as the second "virial" coefficient and may be easily determined at each temperature for which observational data exists. According to (8) the values of B should tend to become linear in T^{-1} as higher temperatures are approached. The figure *3* contains the B data for hydrogen, helium and nitrogen plotted with

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[14] This expression for A is identical with that obtained by Debye, Physik. Z. **21**, 1 (1920).

corresponding values of T^{-1} on the axis of abscissae. Evidently none of these gases appear to be approaching a condition at the high temperatures where B is linear in T^{-1}.[15] On the contrary the helium B coefficients pass through a maximum, while the nitrogen coefficients show a relatively much slighter tendency to curve toward the B axis above 200°. The conclusion to be drawn

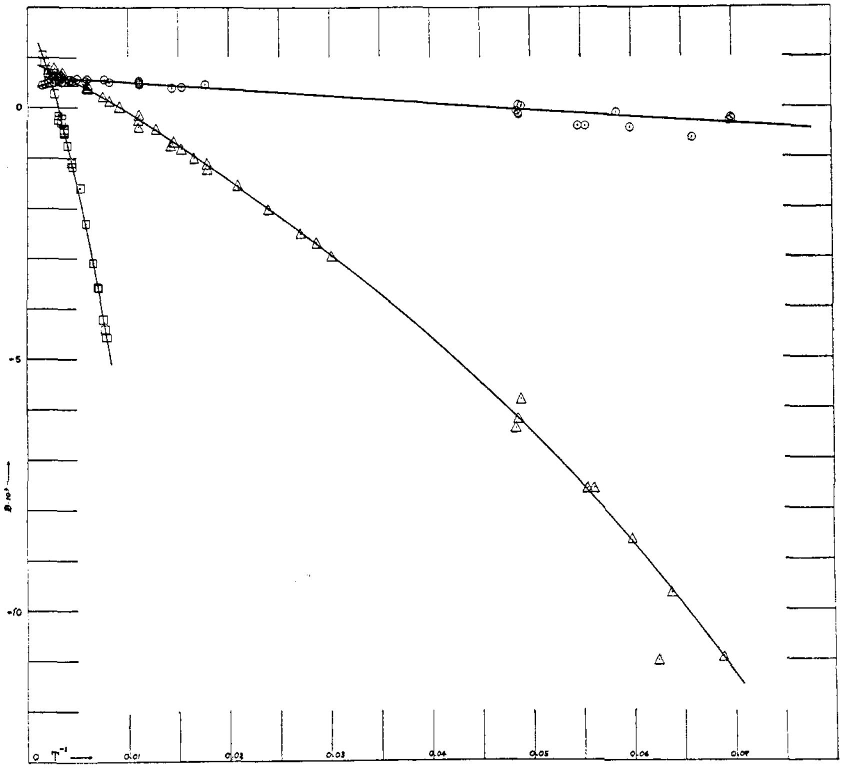

FIG. 3. THE OBSERVED EQUATION OF STATE DENSITY COEFFICIENTS FOR HELIUM ⊙, HYDROGEN △ AND NITROGEN ⊡ RELATED TO TEMPERATURE AS INDICATED BY VAN DER WAALS' EQUATION

The data should be representable by a straight line in the diagram, provided van der Waals' equation was valid.

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[15] This state of a gas, linear relation of B to T^{-1}, may be conveniently denoted as the "van der Waals' state."

is therefore that instead of B approaching the limiting value β for $T^{-1} = 0$ the actual course of the curve may be interpreted to indicate that β becomes progressively smaller with increasing temperature. The case of nitrogen (58) has been discussed elsewhere, but it may be noted that for this gas the magnitude of A relative to β is so large that a correspondingly higher temperature is required to reach a maximum as compared with helium, which has an A value smaller than for any other substance.

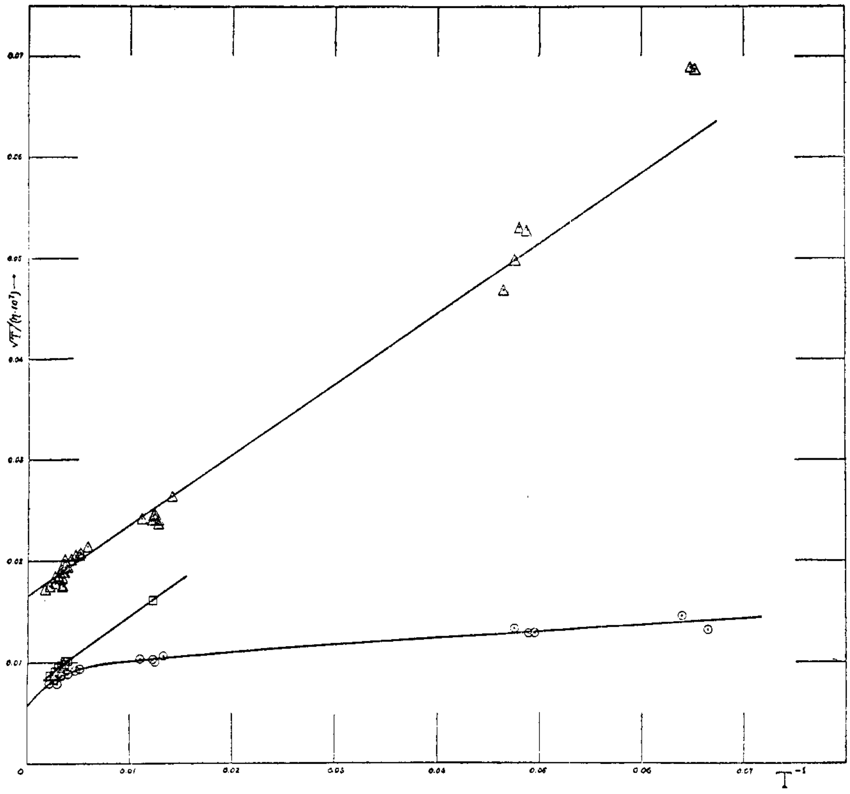

FIG. 4. THE VISCOSITY OF HELIUM ⊙, HYDROGEN ◬, AND NITROGEN ⊡ AS A FUNCTION OF TEMPERATURE ACCORDING TO SUTHERLAND'S FORMULA

It is apropos at this point to examine other data for the purpose of determining whether other experimental facts indicate that the apparent molecular diameter must be regarded as variable with temperature. The viscosity of a gas is a property, the theory of which has been worked out for a van der Waals' molecular model (23). In terms of $\beta = 2/3\ \pi N d^3$ and $A = \frac{6}{5}\pi N^2 \frac{\alpha \tau^2}{d^5}$ the equation may be written as follows; Where M is the molecular weight and k Boltzman's constant.

$$\eta = 3.159.10^{-5} \frac{\sqrt{MT}}{\beta^{2/3}\left(1 + 0.2745 \frac{A}{\beta\, RT}\right)} \tag{9}$$

The latter equation indicates that $\frac{\sqrt{T}}{\eta}$ should be linear in T^{-1} and the data for the three gases used for the discussion above are presented in figure 4. Evidently the viscosity of helium shows no tendency, particularly at high temperatures, to be related to the temperature as indicated by formula (9). Nitrogen on the other hand is tolerably represented and an examination of all available viscosity data indicates that the formula (9) represents the data (19) well, particularly at higher temperatures.

Another model of the molecule for which the viscosity formula has been rigorously derived is that of a point repelling as an inverse power of the distance. The formula taken from Enskog's dissertation is as follows, where a is a number slightly greater than 1, depending only on the index of the distance in the repulsive force formula $\mathrm{F} = \frac{\mathrm{C}}{\mathrm{r}^{\nu}}$, M is the molecular weight, Γ is the gamma function symbol and N is Avogadro's number

$$\eta = a_{\nu}\left(\frac{2\,RT}{NC}\right)^{\frac{2}{\nu - 1}} \frac{15\sqrt{M\,RT}}{16\sqrt{\pi}\,\Gamma\left(\frac{3\,\nu - 5}{\nu - 1}\right)} \tag{10}$$

This formula may be written in the form $\eta = G\ T^{\frac{\nu + 3}{2\,(\nu - 1)}}$ and in figure 5 the values of log η for helium have been plotted with the corresponding values of log T. Evidently the form of the function in (10) suffices to represent the data fairly satisfactorily. The value of ν, the index of the repulsive force may be obtained from slope of the line drawn through the data and is close to 15. The inference which seems to follow is that, at least for helium, the notion of a hard molecule of invariable diameter must be abandoned as a model and replaced by one possessing a repulsive field as well as an attractive field.

The distance of closest approach in a gas phase composed of repelling particles, must vary with the kinetic energy (temperature) as discussed in the first part of the present paper. The equation of state is in fact easily deduced for a low pressure gas whose A constant is small enough to be neglected (helium) at high temperatures.

Proceeding as before to calculate ψ the equation of state is found to be[16]

$$pV = RT + \frac{RT}{V} \frac{\beta_0}{T^{\frac{3}{\nu} - 1}} \tag{11}$$

The equation (11) may be regarded as sufficiently approximate for helium at high temperatures where the attractive term of the order of $\frac{A}{RT}$ is very small by comparison with $\beta_0/T^{3/\nu - 1}$. It is perceived that the logarithm of the B coefficients for helium at the highest temperatures, may be plotted with log T and an estimate thereby obtained of ν. It results that ν is approximately 15 in agreement with the value of the index obtained from a consideration of the viscosity dependence on temperature. The conclusion is supported that the molecular field must be assumed,

[16] $= kT \log (2 \pi mk)^{\frac{3\nu}{2}} [V (V - I) (V - 21) \; . \; . \; . \; .]$

where $I = \int_0^\infty \left(e^{-\frac{\lambda}{\nu - 1} \frac{r^{-(\nu - 1)}}{kT}} - 1 \right) dx\, dy\, dz$

where ν is the index of the distance in the law of repulsive force and λ is a constant involving the constant of repulsive force. The quantity $\beta_0/T^{3/\nu - 1}$ may be considered to be equivalent to $2/3\, \pi N (\bar{d})^3$ where $\bar{d}$ is the apparent diameter of a molecule at definite temperature.

(at least for helium) to possess both an attractive and a repulsive character acting simultaneously.

Further light on the viscosity temperature dependence is obtained by inspecting the formula of J. E. Jones (6), who has

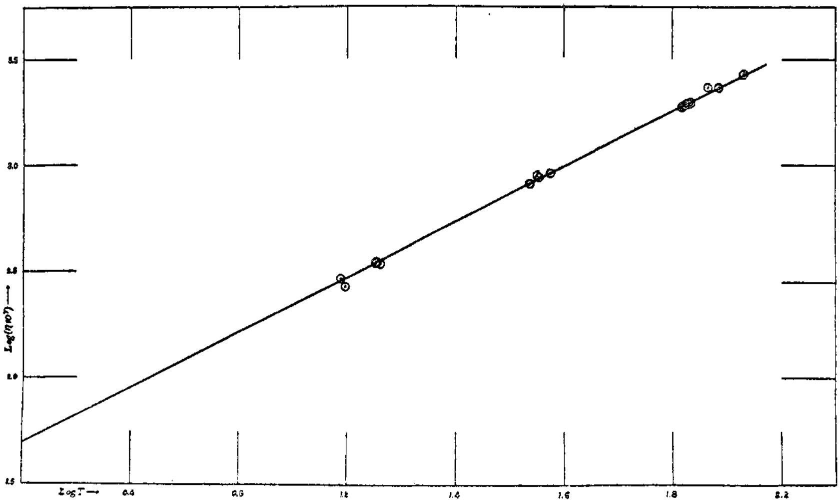

FIG. 5. LOGARITHM OF THE VISCOSITY AS A FUNCTION OF THE LOGARITHM OF THE ABSOLUTE TEMPERATURE FOR HELIUM

developed a formula for the case of a point molecule possessing both attractive and repulsive fields. The formula follows:

$$\eta \propto \frac{\sqrt{T}}{T^{-\frac{2}{\nu - 1}} + \frac{C}{T}} \tag{12}$$

In this formula $T^{1/2}$ is the temperature dependence for the classical molecular model, $T^{-\frac{2}{\nu-1}}$ represents the effect due to the repulsive field while C/T is representative of the attractive field. Evidently when ν is large $T^{\frac{2}{\nu-1}}$ varies slowly at higher temperatures. On the other hand if C is also large (Nitrogen) the temperature dependence will be determined, largely by the term C/T and $\sqrt{T}$. With helium C is very small (4 to 5 units as compared with about 100 for Nitrogen) and consequently the temperature dependence is determined by $T^{-\frac{2}{\nu-1}}$ and $\sqrt{T}$.

The equation of state may be derived by the method used above in which spherically symmetrical attractive and repulsive fields are both assumed. Such a calculation has been carried out by J. E. Jones (59) by a method which fundamentally does not differ from that employed in the present paper. Assuming the molecule to be of the quadruple type and repelling as the inverse fifteenth power, I find the following equation where τ is written for $T^{3/14}$ and β_o and A_o are constants:

$$pV = RT + \frac{RT}{V}\left[\frac{\beta_o}{\tau} - \frac{A_o}{R\,\tau^3} - 0.4638\,\frac{A^2}{R^2\,\beta_o\,\tau^5} - 0.2893\,\frac{A_o^3}{R^3\,\beta_o^2\,\tau^7}\cdots\right] \quad (13)$$

This equation represents the data for helium, hydrogen and nitrogen well at low pressures and high temperatures which is not the case with any equation which predicts a linear increase of pressure with temperature as a limiting condition for temperatures approaching affinity.[17]

The scope of the present paper precludes a complete discussion of the important question of the equation of state of natural dipole gases. The potential energy (attractive) in the case of the later gases must be represented by at least two terms, one representing the potential due to the dipole and the other due to the "induced" polarization as for non polar substances. It may

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[17] Only during the past few years have observations on the p, v, T properties been carried to high temperatures (400°). Previously the data for only a few substances extended even to 200°. With this temperature (200°) as an upper limit it formerly appeared clear that all substances (except helium) were approaching a condition where the pressure increased linearly with temperature. The temperatures at which measurements must be carried out to show the high temperature maximum in the virial coefficient or even a tendency in this direction are higher the larger the value of A or the attractive constant, for the molecule. Thus with nitrogen the effect is just perceptible between 200° and 400°. The temperature in the case of the latter gas at which a maximum would be experimentally demonstrable is estimated to be about 3000°. The theoretical importance of the effect is not, however, of minor importance even in this case, for failure to allow for the effect (temperature variability of apparent molecular diameter) is sufficient above 200° to introduce considerable error in the calculation of pressures.

be remarked, however, that the permanent dipole contribution to the "cohesive pressure" would tend to vanish with temperature increase analogously as in the dielectric constant formula and for the same reasons. The "cohesive pressure" due to the induced polarization would remain operative at all temperatures as indicated by formula (7).

The brief reference to the relation of some of the data to the theoretical formulas for the viscosity and Equation of State derived by the use of very rudimentary and incomplete expressions for the molecular field serve merely as simple illustrations of the far reaching importance of a more exact knowledge of the molecular field. There is indeed scarcely a branch of physical chemistry which would not be benefited by an improved knowledge of the mode of action and properties of these molecular forces.

The explicit discussion attempted above has centered on the conception of a molecular field assumed to be spherically symmetrical. For the equation of state problem, gaseous viscosity, heat conduction, diffusion etc., this assumption is quite justified since the molecules are rapidly rotating and thus the field in its action is "averaged" and consequently is satisfactorily represented by an assumed symmetry. While this condition of assumed symmetry suffices for describing the properties of a *pure* gaseous phase, there are reasons worth considering for supposing the disposition of the field to be unsymmetrical and selective in the case of certain mixtures. How else may the reactive tendency of certain gaseous mixtures be explained, such for example as hydrochloric acid gas and ammonia gas? Also the special facts observed in connection with adsorption, catalytic phenomena and surface tension indicate a very striking selective action in the operation of the molecular field. In the liquid phase also the different solubility phenomena are direct evidence of the highly selective character of the molecular field.

The discussion of light scattering and the Kerr effect has perhaps indicated sufficiently the fact that molecules in general have different properties in different directions. There can scarcely be any doubt that further and more complete investigations of these effects for pure substances and mixtures, for both the gaseous and liquid phase,[18] combined with a correlation of the quantitative results with other physico-chemical data will yield results of the highest interest to the progress of chemistry.

The interesting and important observations relating to surface tensions, particularly the observations made relating to films of the fatty acids etc., are of great interest from the point of view of the molecular field. The development of a quantitative theory of the kinetic kind is, however, extremely difficult. It is safe to say that a flood of light will be thrown on many aspects of the molecular field problem when such a theory is formulated and used to interpret the mass of available data.

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[18] Raman (60) has recently observed a striking phenomenon in the character of the scattered light from pure liquids. The exciting line is found, by photographic means, in the scattered light accompanied by other distinct lines on the longer wave length side. In some cases a line equally distant from the exciting line is found on the short wave length side. The interpretation of the effect is not yet sufficiently advanced to warrant discussion.

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